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(54) Silver halide photographic light-sensitive material and process for preparing a dispersion of discrete particles of water-insoluble polymers in aqueous compositions.

(57) Matting agent dispersions can be obtained having particle size distribution (PSD) not exceeding 10 µm by (1) dissolving in a low-boiling water insoluble organic solvent a polymer, derived from the polymerization through ethylenically unsaturated groups, comprising from 0.05 to 50% by weight of units derived from an ethylenically unsaturated monomer having at least one carboxyl group thereon and from 99.95 to 50% by weight of units derived from ethylenically unsaturated monomers capable of forming hydrophobic homopolymers, (2) adding to the first resulting solution a second solution of an alkali metal compound in water to transform some or all of the carboxyl groups into alkali metal carboxylate groups, and (3) dispersing the second resulting solution in aqueous compositions.

Such matting agent dispersions can be introduced into the coating compositions of the outer light-insensitive layer of a light-sensitive silver halide photographic material without causing either physical or sensitometric harmful effects.

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Silver Halide Photographic Light-Sensitive Material and Process for Preparing a Dispersion of Discrete Particles of Water-Insoluble Polymers in Aqueous Compositions

FIELD OF THE INVENTION

The present invention relates to a silver halide photographic light-sensitive material having incorporated in a gelatin layer thereof discrete particles of a water-insoluble polymeric matting agent and a process for preparing a dispersion of discrete particles of a water-insoluble polymer in aqueous compositions.

BACKGROUND OF THE ART

In the field of photography, water-insoluble matting agents have been used in top or back hydrophilic layers of silver halide light-sensitive materials to prevent adhesion when materials are stored in rolls, cartridges or cassettes in conditions of relatively high humidity and temperature, to prevent electrostatic charges by reducing the area of contact of the photographic material, to prevent the formation of Newton's rings during printing and enlargement, or to decrease the occurrence of scratches during storage or packing of the photographic material.

It is well known in the art that, in order to solve these problems, fine particles of inorganic substances such as silicon dioxide, magnesium oxide, calcium carbonate and the like, or organic substances such as polymethylmethacrylate, cellulose acetate propionate and the like are incorporated as matting agents into the outermost layers of a photographic material. These and other matting agents are described, for example, in US Pat. No. 3,411,907 and British Pat. No. 837,529. Said matting agents are insoluble in alkaline processing solutions and remain in the processed photographic material.

In same cases it is desired to remove the matting agent for the purposes of improving transparency and graininess of the final image. Therefore, matting agents insoluble in neutral or acidic solutions and soluble in alkaline medium have been described in the art. In particular, alkali-soluble matting agents consisting of methacrylic acid - methylmethacrylate copolymers have been described in US Pat. Nos. 2,391,181, 2,992,101, 3,767,448 and 4,142,894, and in British Pat. No. 878,520, and copolymers of styrene and α,β-ethylenically unsaturated carboxy containing monomers have been described in British Pat. No. 1,055,713. Such matting agents are incorporated in the photographic layers in the form of discrete particles by dispersing a solution of the matting agent in a water-immiscible organic solvent in an aqueous gelatin solution, eliminating the organic solvent, and then introducing the obtained dispersion into the coating composition of the photographic layer. Organic solvents or combinations thereof have been studied with the copolymers of methacrylic acid and methylmethacrylate, the basic solvent being butanol and mixture thereof with other solvents. Since butanol is a solvent with low volatility it must be removed by cooling the dispersion and washing with deionized water. Alkali-soluble matting agents consisting of methacrylic acid - ethylmethacrylate copolymers containing from 20 to 50 % by weight of methacrylic acid have been described in US Pat. No. 4,447,525. These copolymers dissolve in high concentrations in high volatile organic solvent such as ethylacetate, a solvent which can be easily removed by evaporation from the dispersion of the polymer in aqueous gelatin.

The matting agents are characterized by the average particle sizes (APS) of their discrete particles and in the patents there are teachings on how to control the APS in the process of synthesis thereof.

Another characteristic of matting agents is their particle size distribution (PSD), in particular the size measure of the higher discrete particles present in the dispersion. Processes described in the art for the synthesis of matting agent dispersions may result in the formation of huge particles exceeding 10 µm of diameter. The presence of such huge particles of matting agents may cause undesirable side effects such as disturbance of uniform coating of the photographic material and disturbance of distinct layer relationship of a plurality of superposed layers of the photographic material.

It is, therefore, strongly desired to develop matting agents, either alkali-soluble or alkali-insoluble, having a PSD not exceeding 10 µm which do not give rise to the above undesirable side effects.

SUMMARY OF THE INVENTION

Matting agents dispersions can be obtained having particle size distribution (PSD) not exceeding 10 µm by (1) dissolving in a low-boiling water insoluble organic solvent a polymer, d rived from the polymerization through ethylenically unsaturated groups, comprising from 0.05% to 50% by weight of repeating units derived from ethylenically unsaturated monomers having at l ast one carboxyl group thereon and from 99.95% to 50% by weight of repeating units derived from ethylenically unsaturated monomers capable of forming hydrophobic homopolymers, (2) adding to the first resulting solution a second solution of alkali metal compound in water to transform some or all of the carboxyl groups into alkali metal carboxylate groups, and (3) dispersing the second resulting solution in aqueous compositions.

According to the scope of the present invention, "carboxyl group" means a group capable to undergo the transformation to alkali metal carboxylate group as, for example, a carboxylic acid, an anhydride and the like.

The matting agent dispersions according to this invention comprise discrete polymeric particles having diameters of maximum 10 µm and comprising from 0 to 49.95 percent by weight of repeating units derived from ethylenically unsaturated monomers having carboxyl groups thereon, from 0.05 to 10 percent by weight of repeating units derived from ethylenically unsaturated monomers having alkali metal carboxylate groups thereon, the sum of units derived from ethylenically unsaturated monomers having alkali metal carboxylate groups thereon and units derived from ethylenically unsaturated monomers having carboxyl groups thereon representing at most 50 percent by weight of the polymer, and the remaining polymer weight percentage derived from ethylenic unsaturated monomers capable of forming hydrophobic homopolymers.

Said matting agent dispersions can be introduced into the coating compositions of the outer light-insensitive layer of a silver halide light-sensitive photographic material without causing either physical or sensitometric harmful effects.

DETAILED DESCRIPTION OF THE INVENTION

Accordingly, the present invention relates to a process for preparing a dispersion of discrete particles of a water-insoluble polymer in aqueous compositions comprising:

(1) dissolving in a low-boiling water-immiscible organic solvent a polymer, derived from the polymerization through ethylenically unsaturated groups, comprising (a) repeating units derived from an ethylenic unsaturated monomer having carboxyl groups thereon, said units comprising from 0.05 to 50 % by weight of said polymer, and (b) repeating units derived from ethylenic unsaturated monomers capable of forming hydrophobic homopolymers, said units forming the remaining polymer weight percentage (99.95 to 50%),

(2) adding to the resulting solution a solution of an alkali metal compound in water in an amount to transform a sufficient number of said repeating units having carboxyl groups thereon into repeating units having alkali metal carboxylate groups thereon, said repeating units, having alkali metal carboxylate groups thereon, comprising from 0.05% to 10% by weight of said polymers, and

(3) dispersing the resulting solution in aqueous compositions.

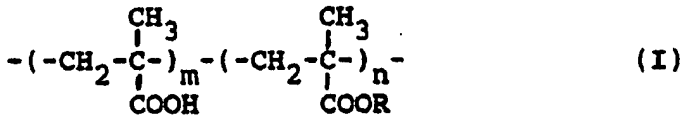
Examples of ethylenic unsaturated monomers having carboxyl groups thereon from which derive the repeating units (a) of the polymer above include acrylic acid, methacrylic acid, maleic acid (including monosubstituted maleates such as monomethyl maleate, monoethyl maleate and monophenyl maleate), itaconic acid (including monosubstituted itaconate such as monomethyl itaconate, monoethyl itaconate and monobutyl itaconate), fumaric acid (including monosubstituted fumarate such as monomethyl fumarate and monoethyl fumarate), crotonic acid, citraconic acid, N-(meth)-acryloylamino acids such as N-acryloylglycine, N-methacryloylglycine, N-acryloylalanine, N-methacryloylalanine and N-acryloylproline, vinylbenzoic acid, maleic acid monoamide, N-alkylmaleic acid monoamides such as N-ethylmaleic acid monoamide and N-butylmaleic acid monoamide, itaconic acid monoamide, N-alkylitaconic acid monoamide such as N-ethylitaconic acid monoamide and N-butylitaconic acid monoamide.

Examples of ethylenic unsaturated monomers from which derive the repeating units (b) of the polymer above include acrylic acid esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate and phenyl acrylate, methacrylic acid esters such as methyl methacrylate, ethyl methacrylate, isopropyl methacrylate and p-chlorophenyl methacrylate, styrenes such as styren , methylstyrene, α-methylstyrene, chloromethylstyrene and bromostyrene, vinyl esters such as vinyl benzoate, vinylphenyl acetat and vinyl naphthoate,

vinyl ethers such as allyl butyl ether, methoxyethyl vinyl ether and phenyl vinyl ether, olefins such as thylene, propylene, 1-butene and 1-pentene, unsaturated nitriles such as acrylonitrile and methacrylonitrile, vinyl ketones such as vinyl methyl ketone and methoxyethyl vinyl ketone, and vinyl chloride.

Of such monomers, methacrylic acid is particularly preferable as the ethylenic unsaturated monomers having carboxyl groups thereon from which derive the repeating units (a) of the polymer above and methacrylic acid esters such as methyl methacrylate and ethyl methacrylate are particularly preferable as ethylenic unsaturated monomers from which derive the repeating units (b) of the polymer above.

Accordingly, the polymer for use in the process of the present invention is preferably represented by the formula (I)



(I)

wherein m represents from 0.05 to 50 % by weight of the polymer, n represents the remaining % by weight of the polymer and R represents methyl or ethyl.

Said polymer is prepared from the polymerization through ethylenically unsaturated groups of the monomers used in the present invention, using any conventional polymerization mechanism, preferably by free radical polymerization. In general, the free radical polymerization is carried out by heating at a proper temperature (which usually does not exceed 100° C and preferably is between 50° C and 100° C) in a proper solvent (usually ethanol or methanol) a mixture of the two monomers in a proper concentration with respect to the solvent (usually at a concentration that does not exceed 40% by weight of the two monomers with respect to the solvent, preferably between 15% to 30%) in presence of a polymerization catalyst (for example of the free radical type, such as benzoyl peroxide or cumene hydroperoxide, or of the azoic type, such as α,α'-azobisisobutyronitrile). The obtained polymer can be then separated from the reaction mixture for example by precipitating into a non-solvent, such as water and drying.

Low-boiling substantially water-immiscible organic solvents for use in the process of the present invention include halogenated hydrocarbons such as chloroform, dichloromethane, carbon tetrachloride, 1,1-dichloromethane, 1,2-dichloroethane and 1,1,1-trichloroethane, aliphatic esters such as ethyl acetate, butyl acetate and isopropyl acetate, aromatic hydrocarbons such as benzene, toluene and xilene, aliphatic hydrocarbons such as pentane and n-hexane, aliphatic ketons such as methyl ethyl ketone and methyl isobutyl ketone, higher aliphatic alcohols such as n-butanol and isobutanol, and the like. Said organic solvents have a boiling point preferably of less than 150° C, more preferably of less than 100° C, and a solubility in water at 20° C preferably of less than 20 grams per liter, more preferably of less than 10 grams per liter.

The alkali metal compounds for use in the process of the present invention are basic compounds able to transform carboxyl groups of the polymer above into alkali metal carboxylate groups. Preferably said basic alkali metal compounds are alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, but other basic alkali metal compounds can be advantageously used such as sodium carbonate, sodium ethoxide, sodium methoxide and the like.

According to the process of the present invention, the organic solution including a polymer comprising (a) repeating units derived from an ethylenic unsaturated monomer having carboxyl groups thereon, said units comprising from 0 to 49.95 % by weight of said polymer, (b) repeating units derived from an ethylenic unsaturated monomer having alkali metal carboxylate groups thereon, said units comprising from 0.05 to 10 % by weight of said polymer, the sum of units derived from an ethylenic unsaturated monomer having alkali metal carboxylate groups thereon and units derived from an ethylenic unsaturated monomer having carboxyl groups thereon representing at most 50 percent by weight of the polymer, and (c) repeating units derived from an ethylenic unsaturated monomers capable of forming hydrophobic homopolymers, said units forming the remaining polymer weight percentage, is dispersed in water. The dispersion is then added with a surface active agent or, preferably, an aqueous hydrophilic colloid solution. The hydrophilic colloid is preferably gelatin, but also gelatin derivatives and other polymeric compounds, such as polyacrylamide and polyvinyl alcohol, can be used. Generally, the organic solvent is eliminated from the dispersion by cooling, noodling and washing the dispersion with pure water or by heating, as known in the art.

The polymers above become dispersed in the aqueous solution of the hydrophilic colloid in the form of fin ly divided particles having diameters from 0.5 to 10 µm with absence of particles having diameters exceeding 10 µm. Said dispersions are introduced into the coating composition of the outer light-insensitive

layer of a silver halide light-sensitive material.

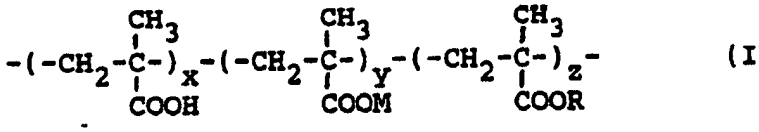
Accordingly, in another aspect, the present invention r lates to a photographic material comprising a support base, one or more light-sensitive. gelatin silver halide emulsion layers and an outer non lightsensitive gelatin layer comprising discrete particles of a water-insoluble polymeric matting agent, wherein said polymeric matting agent comprises:

(a) repeating units derived from an ethylenic unsaturated monomer having carboxyl groups thereon, said units comprising from 0 to 49.95 % by weight of said polymer,

(b) repeating units derived from an ethylenic unsaturated monomer having alkali metal carboxylate groups thereon, said units comprising from 0.05 to 10 % by weight of said polymer, the sum of units derived from an ethylenic unsaturated monomer having alkali metal carboxylate groups and units derived from an ethylenic unsaturated monomer having carboxyl groups representing at most 50 percent by weight of the polymer, and

(c) repeating units derived from an ethylenic unsaturated monomer capable of forming hydrophobic homopolymers, said units forming the remaining polymer weight percentage (99.95 to 50%).

Said water-insoluble polymeric matting agent is preferably represented by the general formula (II)

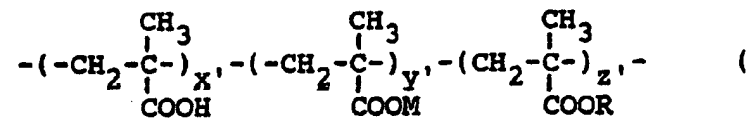


(II)

wherein M represents an alkaline metal, preferably Na and K, R represents methyl or ethyl, x represents from 0 to 49.95% by weight of the polymer, y represents from 0.05 to 10 % by weight of the polymer, x + y represents at most 50 % by weight of the polymer, and z represents the remaining polymer weight percentage.

The maximum percentage by weight of repeating units derived from the ethylenic unsaturated monomer having carboxyl groups thereon in the polymers of the present invention represents the limit beyond which the polymer becomes soluble in neutral or acid aqueous gelatin solutions. By varying the percentage by weight of repeating units derived from the ethylenic unsaturated monomer having carboxyl groups thereon within the limits above, it is possible to control the solubility of the polymeric particles in the alkaline processing solutions for silver halide light-sensitive photographic materials. Total solubility in the alkaline processing solutions for silver halide light-sensitive photographic materials can be approached for polymers having higher percentages of repeating units derived from the ethylenic unsaturated monomer having carboxyl groups thereon, while partial solubility or insolubility can be achieved for polymers having lower percentages of repeating units derived from the ethylenic unsaturated monomer having carboxyl groups thereon.

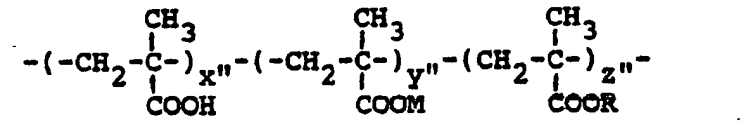
Preferably water-insoluble and alkali-soluble matting agents of the present invention are those comprising discrete particles of a polymer represented by the following general formula (III)



(III)

wherein M represents an alkaline metal, R represents methyl or ethyl, x' represents from 20 to 49.95 % by weight of the polymer, y' represents from 0.05 to 10 % by weight of the polymer, $x' + y'$ represents at most 50 % by weight of the polymer, and z' represents the remaining polymer weight percentage. More preferably, in the formula (III) above R represents an ethyl group.

Still preferably water insoluble and alkali-insoluble matting agents of the present invention are those comprising discrete particles of a polymer represented by the following general formula (IV)



(IV)

wherein M represents an alkalin metal, R represents methyl or ethyl, x'' represents from 0 to 19.95 % by weight of the polymer, y'' represents from 0.05 to 10 % by weight of the polymer, $x'' + y''$ represents at most 20 % by weight of the polymer, and z'' represents the remaining polymer weight percentage.

The matting agents of the present invention are incorporated into the outer layer of the photographic material. They can be for instance incorporated into the surface protective layer coated on the silver halide emulsion layers, or into the backing layer coated on the support base on the side opposite to that containing the light-sensitive layers, or on both sides. It is more preferred, in any case, to incorporate the matting agents of the present invention into outer protective layer.

In the photographic materials of the present invention, the matting agents are incorporated in a quantity of about 50 to about 600 mg., more preferably from about 150 to about 400 mg. per square meter of the surface layer. The binding agent of such layer preferably is gelatin, but treated gelatins like the so-called acid or basic gelatins, the gelatins treated with enzymes, gelatin derivatives and modified gelatins can also be used.

Several additions, such as hardeners, plasticizers, surfactants, antistatic agents, polymeric latexes, anticalcium and antispot agents can be incorporated into said surface layer, as known in the art.

In combination with the matting agents characterized by the water-insoluble and alkali-soluble discrete particles of the polymer represented by the formula (III) above, the surface layer of the photographic material can also contain matting agents characterized by the water-insoluble and alkali-insoluble discrete particles of the polymer represented by the formula (IV) above or water-insoluble and alkali-insoluble discrete particles of matting agents, known in the art, such as for example fine silica, polymethylmethacrylate, starch particles, and the like. Such water-insoluble and alkali-insoluble discrete particles of matting agents are usually used in the outer layer in a quantity lower than that of the water-insoluble and alkali-soluble discrete particles of the polymer represented by the formula (III) above, for instance in a quantity up to 50 mg. per square meter, preferably from 5 to 10 mg. per square meter, since they remain in the photographic material after processing.

Preferably, the matting agents of the present invention can be used in color photographic materials which comprise a plurality of hydrophilic (i. e. permeable to the water photographic processing solutions) emulsion layers containing silver halides dispersed in gelatin, associated with auxiliary hydrophilic gelatin layers, interlayers, antihalo layers, backing layers, said plurality of layers being coated onto a hydrophobic support base.

When used for color reproduction, such silver halide emulsions are sensitive or (sensitized) to the blue and associated with non-diffusing yellow-forming couplers (upon color development with p-phenylene diamine after exposure), or are sensitized to the green and associated with non-diffusing magenta(blue red)-forming couplers, or sensitized to the red and associated with non-diffusing cyan(blue-green)forming couplers.

The photographic element can contain silver halide emulsions, chemical sensitizers, spectral sensitizers and desensitizers, optical brighteners, antifoggants and stabilizers, couplers, acutance dyes, hydrophilic colloids and gelatin substituents, coating aids, hardeners, plasticizers and antistatic agents, as known to the man skilled in the art and can be prepared by following known coating techniques applied to known support bases, as described in Research Disclosure, December 1978, 17643, which is incorporated herein as reference.

The photographic materials of this invention, after exposure, are processed to form a visible image upon association of the silver halide with an alkaline water medium in the presence of a developing agent contained in the medium or in the material, as known in the art. In the case of color photographic materials, the processing comprises at least a color developing bath and, optionally, a pre-hardening bath, a neutralizing bath, a first (black and white) developing bath, etc. These and other baths which complete the photographic processing (e. g. bleaching, fixing, bleach-fixing, intensifying, stabilizing and washing baths) are well-known in the art and are described for instance in Research Disclosure 1978, 17643, incorporated as described above as reference.

The present invention is now illustrated by reference to the following examples.

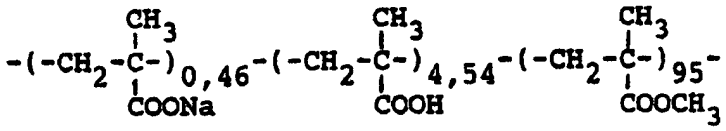
EXAMPLE 1

40 g. (0.46 mole) of methacrylic acid, 760 g. (7.59 moles) of methyl methacrylate, 16 g. of α,α'-azobisisobutyronitril and 3667 ml. of ethyl alcohol were charged into a 3-necked flask. The solution was reflux-heated for 16 hours. The obtained polym r was then precipitated by pouring th alcoholic solution

into a large volume of water under vigorous stirring. The separated polymer was filtered, washed with water and dried at 60° C in the air. The yield was 775 g. (97% of the theoretic yield). The methacrylic acid weight content in th polymer was 5%. The polymer was soluble up to 40% by weight in ethyl acetate.

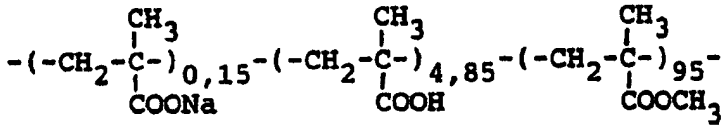
EXAMPLE 2

To 235 g. of a 30% by weight ethyl acetate solution of the polymer of example 1 were added under stirring 3 ml. of sodium hydroxide 1N. After ten minutes stirring the solution was dispersed with a very fast homogenizer (L2R homogenizer sold by Silversen Ltd.) in 250 ml. of a water solution containing 1% by weight of polyvinylalcohol (Mowiol® 4-98) and saturated with ethyl acetate. After five minute homogenizing, 352 g. of 10% by weight gelatin water solution and 340 ml. of water were added to the emulsion under stirring. The obtained dispersion (Dispersion A) contained discrete particles of a polymer corresponding to the formula:

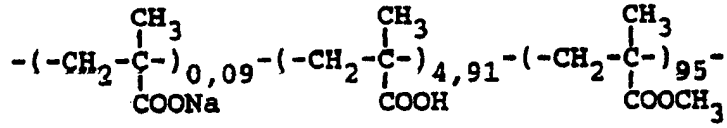


Following the procedure described above Dispersion B and C were prepared using, respectively, 1 ml. and 0.6 ml. of sodium hydroxide 1N and containing discrete particles of a polymer corresponding to the formulas

(Dispersion B):



(Dispersion C):



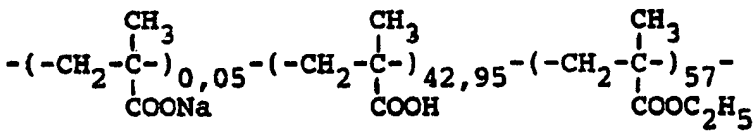
EXAMPLE 3

360 g. (4.18 moles) of methacrylic acid, 440 g. (3.86 moles) of ethyl methacrylate, 32 g. of α,α'-azobisisobutyronitrile and 4,000 ml. of ethyl alcohol were charged into a 3-necked flask. The solution was reflux-heated for 17 hours. The obtained polymer was then precipitated by pouring the alcoholic solution into a large volume of water under vigorous stirring. The separated polymer was filtered, washed with water and dried at 60° C in the air. The yield was 742 g. (93% of the theoretic yield). The methacrylic acid weight

content in the polymer was 43%. The polymer was soluble up to 25% by weight in ethyl acetate saturated with water (5%).

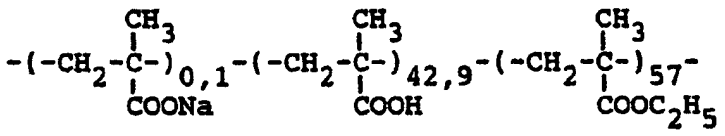
EXAMPLE 4

To 160 g. of a 25% by weight ethyl acetate-water (95:5) solution of the polymer of example 3 were added under stirring 8 ml. of methyl alcohol and 0.2 ml. of sodium hydroxide 1N. After ten minutes stirring the solution was dispersed with a very fast homogenizer (L2R homogenizer sold by Silverson Ltd.) in 160 ml. of a water solution containing 1% by weight of polyvinylalcohol (Mowiol® 4-98) and saturated with ethyl acetate. After five minute homogenizing, 200 g. of 10% by weight gelatin water solution and 136 ml. of water were added to the emulsion under stirring. The obtained dispersion (Dispersion D) contained discrete particles of a polymer corresponding to the formula:

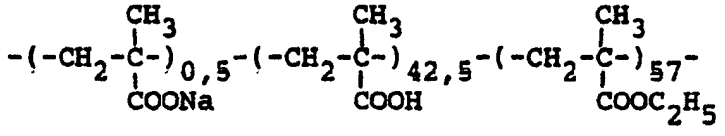


Following the procedure described above Dispersion E and F were prepared using, respectively, 0.4 ml. and 2.0 ml. of sodium hydroxide 1N and containing discrete particles of a polymer corresponding to the formulas

(Dispersion E):

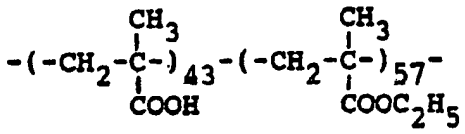


(Dispersion F):



EXAMPLE 5

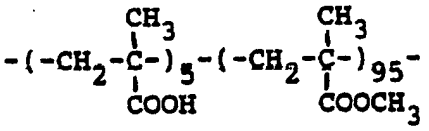
160 g. of a 25% by weight ethyl acetate-water (95:5) solution of the polymer of example 3 were dispersed with a very fast homogenizer (L2R homogenizer sold by Silverson Ltd.) in 160 ml. of a water solution containing 1% by weight of polyvinylalcohol (Mowiol® 4-98) and saturated with ethyl acetate. After five minute homogenizing, 200 g. of 10% by weight gelatin water solution and 136 ml. of water were added to the emulsion under stirring. The obtained dispersion (Dispersion G) contained discrete particles of a polymer corresponding to th formula:



Following the procedure described above Dispersion H was prepared using a n-butanol solution instead of the ethyl acetate-water solution.

EXAMPLE 6

235 g. of a 30% by weight ethyl acetate solution of the polymer of example 1 were dispersed with a very fast homogenizer (L2R homogenizer sold by Silverson Ltd.) in 250 ml. of a water solution containing 1% by weight of polyvinylalcohol (Mowiol® 4-98) and saturated with ethyl acetate. After five minutes homogenizing, 352 g. of 10% by weight gelatin water solution and 340 ml. of water were added to the emulsion under stirring. The obtained dispersion (Dispersion I) contained discrete particles of a polymer corresponding to the formula:



EXAMPLE 7

Onto a subbed cellulose triacetate support bases were coated, in succession, an antihalation gelatin layer, a low-sensitivity red-sensitive silver halide emulsion layer, a high-sensitivity red-sensitive silver halide emulsion layer, a gelatin interlayer, a low-sensitivity green-sensitive silver halide emulsion layer, a high-sensitivity green-sensitive silver halide emulsion layer, a yellow filter gelatin layer, a low-sensitivity blue-sensitive silver halide emulsion layer, a high-sensitivity blue-sensitive silver halide emulsion layer and an uppermost gelatin layer to produce Samples 1 to 9. Each uppermost layer comprised gelatin added with the dispersions reported in the following Table 1 to have 0.5% in weight respect to gelatin of polymer particles as matting agents.

The surface of each sample was observed under a microscope (a Photomicroscope 3 manufactured by Zeiss) equipped with a 414004 micrometric reticle manufactured by Zeiss to evaluate the size limits, the absolute number of particles and the number of particles higher than 2.5 μm and 4 μm per square centimeter.

TABLE 1

Sample	Dispers.	Size Limit	Number of Particles x $10^6/cm^2$		
		(μm)	Abs.	>2.5μm	>4μm
1 (Inv.)	A	0.5 to 6	10.4	0.63	0.046
2 (Inv.)	B	0.5 to 8.5	3.3	0.44	0.11
3 (Inv.)	C	0.5 to 10	2.5	0.45	0.19
4 (Inv.)	D	0.5 to 10	5.6	0.28	0.084
5 (Inv.)	E	0.5 to 8	7.8	0.39	0.073
6 (Inv.)	F	0.5 to 6	17.2	0.5	0.033
7 (Comp.)	G	0.5 to 16	6.9	0.27	0.085
8 (Comp.)	H	0.5 to 18	1.2	0.07	0.039
9 (Comp.)	I	0.5 to 26	0.78	0.14	0.052

Claims

1. A process for preparing a dispersion of discrete particles of a water-insoluble polymer in aqueous compositions comprising:

(1) dissolving in a low-boiling water-immiscible organic solvent a polymer, derived from the polymerization through ethylenically unsaturated groups, comprising (a) repeating units derived from an ethylenic unsaturated monomer having carboxyl groups thereon, said units comprising from 0.05 to 50 % by weight of said polymer, and (b) repeating units derived from ethylenic unsaturated monomers capable of forming hydrophobic homopolymers, said units forming the remaining polymer weight percentage (99.95 to 50 %),

(2) adding to the resulting solution a solution of an alkali metal compound in water in an amount to transform a sufficient number of the repeating units having carboxyl groups thereon into repeating units having alkali metal carboxylate groups thereon, said repeating units, having alkali metal carboxylate groups thereon, comprising from 0.05% to 10% by weight of said polymers, and

(3) dispersing the resulting solution in aqueous compositions.

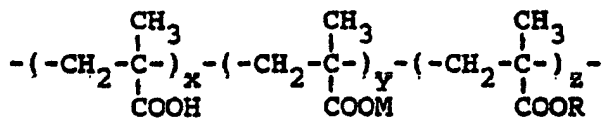
2. A photographic material comprising a support base, one or more light-sensitive gelatin silver halide emulsion layers and an outer non light-sensitive gelatin layer comprising discrete particles of a water-insoluble polymeric matting agent, wherein said polymeric matting agent comprises:

(a) repeating units derived from an ethylenic unsaturated monomer having carboxyl groups thereon, said units comprising from 0 to 49.95 % by weight of said polymer,

(b) repeating units derived from an ethylenic unsaturated monomer having alkali metal carboxylate groups, said units comprising from 0.05 to 10 % by weight of said polymer, the sum of units derived from an ethylenic unsaturated monomer having alkali metal carboxylate groups and units derived from an ethylenic unsaturated monomer having carboxyl groups representing at most 50 percent by weight of the polymer, and

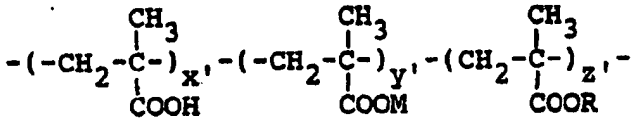
(c) repeating units derived from an ethylenic unsaturated monomer capable of forming hydrophobic homopolymers, said units forming the remaining polymer weight percentage (99.95 to 50%).

3. A photographic material as claimed in claim 2, wherein said polymeric matting agent is represented by the following general formula



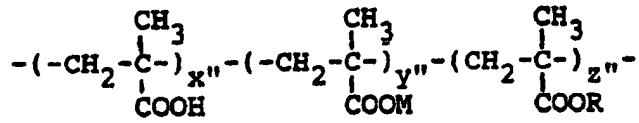
wherein M represents an alkaline metal, R represents methyl or ethyl, x represents from 0 to 49.95 % by weight of the polymer, y represents from 0.05 to 10 % by weight of the polymer, x + y represents at most 50 % by weight of the polymer, and z represents the remaining polymer weight percentage.

4. A photographic material as claimed in claim 2, wherein said polymeric matting agent comprises water-insoluble and alkali-soluble discrete particles and is represented by the following general formula



wherein M represents an alkaline metal, R represents methyl or ethyl, x' represents from 20 to 49.95 % by weight of the polymer, y' represents from 0.05 to 10 % by weight of the polymer, $x' + y'$ represents at most 50 % by weight of the polymer, and z' represents the remaining polymer weight percentage.

5. A photographic material as claimed in claim 2, wherein said polymeric matting agent comprises water-insoluble and alkali-insoluble discrete particles and is represented by the following general formula



wherein M represents an alkaline metal, R represents methyl or ethyl, x'' represents from 0 to 19.95 % by weight of the polymer, y'' represents from 0.05 to 10 % by weight of the polymer, $x'' + y''$ represents at most 20 % by weight of the polymer, and z'' represents the remaining polymer weight percentage.

6. A photographic material as claimed in claim 4, additionally comprising water-insoluble and alkali-insoluble discrete particles of a polymer represented by the general formula of claim 5.

7. A photographic material as claimed in claim 2, wherein the polymer particles are substantially in form of beads having diameters from 0.5 to 10 µm.

8. A photographic material as claimed in claim 2, wherein the polymer particles are present in said outer layer in an amount of from 50 to 600 mg. per square meter.

9. A photographic material as claimed in claim 2, wherein the outer gelatin layer containing said discrete polymer particles is an outer protective layer coated on a light-sensitive gelatin silver halide emulsion layer.

10. A photographic material as claimed in claim 2, wherein the gelatin light-sensitive silver halide emulsion layers are sensitized to different regions of the visible spectrum and associated with dye forming couplers.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 12 1311

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X,Y	GB-A-1 291 392 (E.I. DU PONT DE NEMOURS AND CO.) * Whole document *	1,2-10	G 03 C 1/95
Y,D	US-A-4 447 525 (A. VALLARINO et al.) * Whole document *	2-10	
A	GB-A-2 078 992 (FUJI PHOTO FILM CO. LTD) * Whole document *	2-10	
A	US-A-3 296 172 (D.L. FUNCK et al.) * Whole document *	1	
A	US-A-4 094 848 (K. NAITO et al.) * Whole document *	2-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

G 03 C
C 08 J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10-01-1990	BOLGER W.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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